Degradation of acetylene in a non thermal plasma pulsed discharge at atmospheric pressure

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Abstract: Combined experimental and modeling studies of acetylene oxidation in pulsed corona discharges working in the nanosecond regime are presented. The corona cell was characterized in term of power deposition to provide input data for the model. The concentrations of ozone, CO, CO\textsubscript{2} and residual acetylene were systematically measured for model validation purposes. The model used allows describing the detailed chemistry in the discharge and the mass transfer between the microdischarges and the discharge free regions in the corona cell.

Keywords: corona discharge, atmospheric pressure, acetylene, modeling

1. General

Atmospheric non thermal plasmas (ANTP) show a high potentiality as efficient tools for the advanced oxidation of volatile organic compounds (VOC) in flue gases.

The oxidation process was evaluated for several model VOC’s in terms of energy cost (the so called b factor), residual fraction of the considered VOC and selectivity in CO and CO\textsubscript{2} [2, 4]. There is however very little information on the whole picture of the oxidation process and especially on the mechanisms and the product distributions of VOC’s oxidation in ANTP’s.

In this paper, we are interested in a detailed investigation of the oxidation kinetics of a model VOC, acetylene, in a pulsed corona system working in the nanosecond regime. Our choice of acetylene was motivated by the fact that the oxidation of this species under atmospheric discharge conditions was little investigated despite its key-role in soot generation and its presence among other small molecules in mobile exhausts [1–3]. Our aim is to understand how the processes that take place over a very short time-scale (50–100 ns) in very small filamentary micro-discharges (100 µm) induce the macroscopic change observed on the composition of a gas mixture flowing during several minutes in an active corona reactor with a volume of few tens of cm\textsuperscript{3}. Our purpose is also to identify the different oxidation channels in the discharge, to determine the weight of these channels in the observed discharge oxidation efficiency, and to determine the oxidation product distributions as function of the discharge parameters.

2. Experimental setup

The discharge is generated by a Marx generator allowing reaching 20-30kV voltage on the cathode [4]. The experimental setup is presented in the Figure 1.

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The gas inlet is mainly composed by a N\textsubscript{2}/O\textsubscript{2} mixture containing 5% in oxygen added with 500 ppm of acetylene. Gas flow rate is fixed at 100 mL/min corresponding to a residence time in the reactor of around 30 sec.

Measurements of the CO, CO\textsubscript{2} and residual acetylene concentration have been realised in the cell outlet. Gas chromatography analysis has been used to measure residual acetylene and identify the by-products. Fourier Transform Infrared Spectroscopy has also been used to identify by-products. A continuous monitoring of CO and CO\textsubscript{2} concentration has been achieved using an electrochemical analyzer and a non-dispersive infra-red analyser.

Ozone concentration was determined online by FTIR absorption spectroscopy using the absorption band at 1 045 cm\textsuperscript{-1}. An iodometric method was used to calibrate the FTIR measurements.

![Fig 1: experimental setup](image)

The energy deposition of the investigated discharge was evaluated through the specific input energy, SIE. This is the energy deposited per unit volume of gas in the discharge cell. It is obtained from the discharge pulse frequency, the energy deposited per pulse and the gas flow rate using the expression:

\[
\text{SIE (J L}^{-1}) = \frac{\text{Pulse energy (mJ)} \times \text{Frequency (Hz)} \times 60}{\text{Flow rate (mL min}\textsuperscript{-1})}
\]
The energy deposited during one discharge pulse is estimated from the measured current and voltage. Figure 2 shows typical voltage and current waveforms associated to the pulsed corona discharge. Voltage and current reach respectively 20 kV and 35 A after 10 ns.

The typical value for the energy deposited in the discharge ranges between 20 mJ and 60 mJ per pulse, which corresponds to an average power of 3 W at 10 Hz.

3. Reactor model

A quasi-homogeneous chemical model is proposed for the oxidation of acetylene. It takes into account two types of region: the filamentary volumes where discharges take place, and the region outside these volumes.

The model used here assumes that the electrical energy is uniformly deposited in the volume of a single discharge, that the species concentrations are uniform over the discharge and post-discharge volumes, and that a diffusion driven mass transfer takes place between the filamentary discharge region and the surrounding regions.

The model takes into account 86 species containing C, N, O and H atoms involved in 421 reactions [5] and allows to describe the detailed chemistry in the discharge and the mass transfer between the microdischarges and the discharge free regions in the corona cell.

A complete description of the model will be presented in the poster.

4. Results and discussion

Figure 3 illustrates the calculated time evolution of active species N, O, OH, electron and electron temperature during a period of pulse of 25 ms in a single discharge.

During the 50 ns discharge pulse, O atoms and OH radicals increase exponentially to reach $10^{17}$ and $10^{13}$ cm$^{-3}$ respectively. The OH radical keeps increasing up to $10^{18}$ cm$^{-3}$ after 30 µs, while O atoms are still two orders of magnitude higher.

O atoms are produced in the discharge by electron-impact dissociation and consumed mainly through the formation of ozone (three body recombination process) and to a less extend through the oxidation of acetylene.

Ozone concentration is almost constant during the discharge pulse (50 ns), i.e. about $10^{15}$ cm$^{-3}$. It starts increasing after 30 µs, time which corresponds to the depletion of O through three body recombination. The ozone depletion at higher time is due to the mass transfer between the filamentary discharge and the surrounding gas.

Acetylene concentration is almost constant during the first microsecond, and its degradation takes place over 100 microseconds.

The removal kinetic of acetylene will be largely described in the poster. We can just note that acetylene degradation is mainly due to its reaction with atomic oxygen. This reaction produces ketene and CO radical. The increase of the acetylene concentration at the end of the period is due to the mass transfer between the filament and the surrounding area.

Figure 4 illustrates the time-variations during a single discharge period of the densities for the most abundant stable species produced in the discharge.

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Major assumptions of the model, as well as reaction pathways, will be largely discussed during the poster session.
Figure 5 shows the evolution of the space-averaged acetylene concentration as a function of the residence time for a 15 mJ energy pulse and a 40 Hz repetition rate. We denote “space-averaged concentration” the concentrations averaged over one discharge filamentary volume and the associated discharge free volume.

The acetylene space-averaged concentration decreases from 500 ppm to 150 ppm between 0 and 17 s. CO and CO$_2$, the main by-products that results from the oxidation of C$_2$H$_2$, increase with time and reach respectively 500 ppm and 150 ppm at 17 s. i.e. Ketene (CH$_2$CO), and formaldehyde (CH$_2$O) show different trends. Ketene density reaches a maximum of 100 ppm, while formaldehyde density remains much smaller with a maximum value below 20 ppm. It appears therefore that for a long enough residence time ketene and formaldehyde are converted in the discharge;

The figure 6 presents the comparison between the acetylene residual concentration calculated and measured at the exit cell. The experimental and calculated results present a very good similarity. When the residual fraction of acetylene varies exponentially with the specific input energy SIE, the discharge efficiency for VOC’s conversion (namely $\beta$) may be evaluated through the energy cost b which is obtained from the slope of the variation of logarithm of the residual acetylene as function of SIE [5]. The $\beta$ calculated by the model is equal to 280 J/L, while the $\beta$ measured experimentaly is at 250 J/L.

Figures 7 and 8 present respectively the comparison between the CO and CO$_2$ yield (%), calculated and measured at the cell exit. The predicted and measured CO yields are in good agreement with 12 %, and represent almost 50 % of the converted acetylene.

The agreement between the calculated and measured CO$_2$ yield is less satisfactory. The main sources of differences will be discussed in the poster.

5. Conclusion.
This paper deals with the comparison between experimental and modeling studies of acetylene oxidation in pulsed corona discharges working in the nanosecond regime are presented. A quasi-homogeneous model is described. Acetylene removal as well as sub-products concentrations calculated and measured are compared. Major reaction paths are discussed and validated by experimental measurements.

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7. References.